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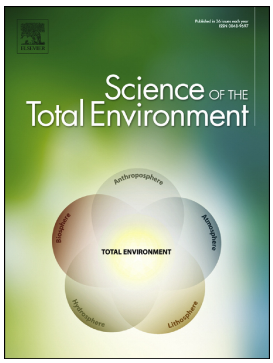

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Spatio-vertical characterization of the BTEXS group of VOCs in Chinese agricultural soils

Chenye Xu,[a,b] Xinmeng Lin,[b] Shanshan Yin,[b] Kai Liu,[c] Weiping Liu,[b*]

[a] College of Environmental Science and Engineering, Donghua University, Shanghai, 201620, China

[b] Ministry of Education Key Laboratory of Environmental Remediation and Ecosystem Health, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, China

[c] Division of Engineering and Applied Science, W. M. Keck Laboratories California Institute of Technology, 1200 East California Blvd., Pasadena, California 91125, USA

[*]Corresponding author:

E-mail addresses: wliu@zju.edu.cn (W. Liu)

ABSTRACT

Ubiquitous contamination of the BTEXS (benzene, toluene, ethylbenzene, xylene, and styrene) group in soils is a significant concern for ecological safety. However, comprehensive spatio-vertical survey of the BTEXS group on a national scale is rare to date. Using a static headspace gas chromatography-mass spectrometry method (HS-GCMS), this study performed a quantitative analysis of BTEXS levels in soils from Chinese rural areas in 2013 and 2016. The median ∑BTEXS concentrations in surface soils in 2013 and 2016 were 37.5 and 34.4 ng/g dry weight, respectively. Toluene was the dominant pollutant, accounting for approximately 41.6 % and 32.1 % of the total levels. BTEXS contamination was higher in Shanxi province, Northeast China, and Yunnan-Guizhou Plateau compared to the other regions. Vertically, toluene, *m,p'*-xylene and *o'*-xylene concentrations were significantly higher in the top soil layer (0-15 cm) and decreased significantly with increasing soil depth ($p < 0.05$). Higher soil organic matter was significantly associated with higher BTEXS concentrations of sampling site. BTEXS was also enhanced at sites with higher elevations and lower temperature due to global distillation effects. The findings of this study could help decision-makers to protect against BTEXS contamination in rural areas. These findings provide a basis for further study of the mechanism of BTEXS migration and transport in large-scale environment.

Capsule: Spatio-vertical distribution, influence factors, exposure risks of BTEXS in soils from Chinese agricultural region was studied.

Key words: BTEXS; National spatio-vertical distribution; potential influencing factors

INTRODUCTION

Contamination of soil by volatile organic compounds (VOCs) has become a significant environmental issue worldwide due to the toxicity and widespread occurrence of VOCs. The acronym BTEXS refers to the combination of benzene, toluene, ethylbenzene, xylenes (*ortho, meta, and para*) and styrene, which constitute more than 60 % of non-methane VOCs worldwide (Alghamdi et al., 2014). Benzene is a Group 1 carcinogen defined by the World Health Organization (WHO, 1999). Toluene and xylene are included in List 2 of the potentially toxic compounds by Health Canada (Health Canada, 2006). Benzene, toluene, and ethylbenzene are designated as "priority pollutants" by the U.S. Environmental Protection Agency (U.S. EPA, 2012). BTEXS exposure risks are well defined, with BTEXS exposure known to cause cancer, respiratory problems, skin irritation, central nervous system depression, and endocrine disruption in humans (Bolden et al., 2015).

Although the accurate determination of BTEXS in soil samples is hampered due to matrix complexity and the volatility of the target compounds, numerous studies have developed quantitative analysis methods with environmentally friendly pretreatment techniques (Pinto et al., 2011). Solvent-minimized methods, including headspace (Serrano and Gallego, 2006), purge-and-trap (Campillo et al., 2004), and solid-phase micro extraction techniques (Fromberg st al., 1996) have been widely employed to replace the classical but time-consuming Soxhlet or liquid-solid extraction method (Pinto et al., 2011). In 2017, Varona-Torres et al., were the first to utilize RTILs 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][ESO4], 1-ethyl-3-methylimidazolium diethyl phosphate [EMIM][DEP], and tris(2-hydroxyethyl) methylammonium methylsulfate [MTEOA] [MeOSO3] as headspace solvents to normalize the matrix effects from BTEX measurement in soils.

This method had improved sensitivity and accuracy and the findings demonstrated that matrix effects can be normalized across soil textures (Varona-Torres et al.,2017). These novel methods offer environmental and economic advantages (Serrano and Gallego, 2006).

Soils serve as a gigantic reservoir and secondary source for environmental contaminants. There are an increasing number of regional-scale surveys of BTEXS residue in soils (Du et al., 2011; Fromberg et al., 1996; Serrano and Gallego, 2006; Shin et al., 2012; Yao, 2016; Zhang et al., 2012; Zhou et al., 2013). Results from former chemical plant site in Jilin, China (Zhou et al., 2013), pesticide production site in Changzhou, China (Yao, 2016; Zhang et al., 2012), petroleum hydrocarbons contaminated soils in Korea (Shin et al., 2012) and selected agricultural soils in Mediterranean areas (Serrano and Gallego, 2006) suggest that the BTEXS group are a product of both anthropogenic and biogenic sources (Bolden et al., 2015). Direct determination and modeling predictions have documented BTEXS transportation in soils and emission from soil to air (Du et al., 2011). These observations are of great concern with respect to atmospheric contamination and population exposure.

While multiple studies have conducted field measurements of BTEXS in soils and the soil-air interface, the area covered in China is scarce and sporadic. In addition, there is a scarcity of information regarding the vertical distribution of BTEXS in the soil column; sampling data from different soil layers would provide more information on environmental trends in the soil environment. To the best of our knowledge, systematic evaluation of the spatial and vertical distribution of BTEXS, and associated risk assessment, in agricultural soils remains limited.

By establishing a sensitive and reliable headspace method with a gas chromatograph-mass spectrometer system (HS-GCMS), we analyzed the BTEXS

group in agricultural soil samples collected throughout China. We aimed to comprehensively characterize the spatial and vertical distribution of BTEXS and elucidate the influences of natural conditions and anthropogenic activity on their distributions. The results of this study can make a pioneering contribution to our understanding of the occurrence and outcomes of BTEXS contamination across China and can provide guidance and support to policymakers for more effective pollutant control.

MATERIALS AND METHODS

Samples Collection

A total of 227 surface soil samples were collected from 30 regions in four large geographic areas across China, including 116 samples from between April and May 2013, and 111 samples in May 2016 (Fig. S1 of Supporting Information (SI)). Core samples (n = 150) from 2016 were categorized as surface (0-15 cm), middle (15-30 cm) and bottom (30-45 cm) segments (Fig. S2). All sites were agricultural fields and located by global positioning system, and geographical coordinates of soil sampling points were displayed in (Table S1). Soil was collected after the overlying vegetation was thoroughly removed. Each sample was placed into a sealed aluminum foil bag and was transported in a timely manner back to the laboratory. Samples were stored at -20℃ before analysis.

Analytical Procedure

The experimental setup consisted of a headspace autosampler (HP 7694) and a gas chromatograph (Agilent 7890B) equipped with a mass spectrometer (Agilent 5977A) operated in the electron impact (EI) mode. The extraction procedures and

analysis methods for the target compounds were performed according to the U.S. EPA method 5021, with modification (U.S. EPA, 2014). Briefly, after each sample was homogenized and sieved through a 60 mesh sieve, 2 g of the sample was placed into a 22 mL crimp-seal headspace vial. 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4 were added as the surrogates. 10 mL of matrix modifying solution was added to each soil sample to act as a chemical preservative. Then the hermetic vials were placed in the autosampler carousel of the headspace analyzer.

Aliquots of 1 μL were injected into the Rtx-1 Cap. Columns (two columns connected: RTX-1 60 m + RTX-1 30m , 0.32 mm i.d., 1.5 mm film thickness; Shimadzu Corporation) with a split ratio of 10:1. The optimized gas chromatography process cannot separate *m'*-xylene and *p'*-xylene, therefore we used the sum concentrations of them in this study. The temperature program of the GC-MS analysis was as follows: initial temperature of 50 ℃, increased at 10 ℃ min^{-1} to 230 ℃, held for 7 min. The injector temperature was kept at 250 ℃. The carrier helium gas was kept at a constant flow rate of 1 mL min^{-1}. BTEXS were quantified using the selected ion mode (SIM). The target ions were *m/z* 77, 78 for benzene, 91, 92 for toluene, and 91, 106 for ethylbenzene, xylene, and 103, 104 for styrene, one ion was chosen as the quantifier, the others were used as qualifier.

Environmental Parameters

The elevations of the sampling sites were measured at the time of sampling. Data on annual average temperature and precipitation, were collected from the China Statistical Yearbook (National Bureau of Statistics of China, 2013). The total organic carbon content in the soil samples was determined based on a reported method (Lu, 2000). Soil pH was analyzed by a glass PH electrode in a 1:2.5 (grams of soil/mL of

Milli-Q water) mixture (Leff and Fierer, 2008).

Quality Assurance and Quality Control

The analytical standard mixture of benzene, toluene, ethylbenzene, *m'*-xylene, *p'*-xylene, *o'*-xylene, styrene, and surrogate standards of 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4 was purchased from J&K Chemical Ltd. (Beijing, China). Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Methanol and phosphoric acid were of high performance liquid chromatography (HPLC) grade. Sodium chloride of ACS reagent grade was activated at 400 ℃ for 4 hours before use.

Quality control criteria were complied with to achieve correct identification and quantification of BTEXS during all the analytical procedures. Glass apparatuses were cleaned and heated overnight before use. All instruments in contact with the samples were interference-free. Procedural blank samples were analyzed after every 10 soil samples to check the potential interference and contamination. A trip blank was carried through sampling and handling protocols, serving as a check for such contamination. Surrogates were added to each field and QC sample; their recoveries were monitored to evaluate the effects of the sample matrix. The method blank, trip blank, and matrix spike samples were subjected to the same analytical procedures as those used for the real samples. Chromatogram of selected ions in standard solution was depicted in Fig. S3. Six peaks were clearly separated according to the GC/MS conditions mentioned above. The calibration curve of each substance was plotted with the peak area as the ordinate and concentration as the abscissa (Table S2). The limit of detection (LOD) and limit of quantification (LOQ) were determined as three times and ten times the signal-to-noise ratio, respectively. The method detection limit (with all steps of the analysis included, MDL) was estimated using the following equation:

$$MDL = 3.143\delta \quad (1)$$

where δ is the standard deviation of the peak area for 7 replicates (n = 7) near the expected limit of detection, and 3.143 is Student's factor (n−1, 0.99). The detection limit with this method ranged from 0.034 to 0.175 ng/g. The recoveries of BTEXS in spiked samples ranged from 69.2 to 107 %. Detailed LOD, LOQ, MDL and recovery results are shown in Table S3. Duplicate samples were detected during the analysis.

Data Analysis

Before analysis, values below the LOD were replaced by LOD/$\sqrt{2}$. Spatial distributions of BTEXS in Chinese agricultural soils were depicted by geographic information system (GIS) mapping software (ArcGIS 9.3, ESRI, Redlands, California) with the Kriging method used for interpolation of BTEXS levels between different locations. The results were normalized to the distribution for further statistical analysis. Pearson correlations with one-way analysis of variance (ANOVA) and Student T-tests were employed in potential source analysis. Correlations were defined as statistically significant at the *p*-value of 0.05 (2-tailed). All data were analyzed using SPSS software (version 16.0, SPSS Inc., Chicago, IL, USA).

RESULTS AND DISCUSSION

Optimization of Method Parameters for Determination of BTEXS in Soils by HS-GC/MS

Method optimization was principally carried out with respect to the selection of equilibrium time, oven temperature, and matrix modifying solutions. Sampling time has an important effect on the method efficiency for maximum sensitivity is obtained at equilibrium reaches between solution in the sample and headspace gas phase.

Chromatographic peak areas of BTEXS at different equilibrium times (10, 20, 30, 40, 50 min) are shown in Fig. 1(a). The maximum peak areas of all BTEXS appeared at 30 min. Shorter incubation times led to lower signals, while longer incubation times may cause partial degradation (Shin et al., 2012). Oven temperature is also a critical parameter for method sensitivity as it is directly related to vapor pressure, which affects the distribution coefficient between the two phases. Fig. 1(b) illustrates the individual BTEXS chromatographic peak areas at different headspace oven temperatures. The sample incubation process can reduce the solubility of VOCs in the formation of the gas phase. The highest peak area was obtained at 70℃. With continued increases in temperature, the signal began to decrease. This can be attributed to the increased moisture content in the gas phase under excessively high temperatures; this lowers the percentage of ionized target analytes and shortens the life expectancy of the chromatographic column (Fakhari et al. 2012). Fig. 1(c) shows the effect of ionic strength on BTEXS determination (0, 5, 10, 20, and 26% of NaCl in 10 mL solutions). An increase in ionic strength can decrease BTEXS solubility and stimulate volatilization into the headspace phase (Pascale et al., 2018). As saturation (26 %) of sample produced the best results in enhancing the analysis sensitivity for BTEXS, the saturated NaCl solution was used for HS sampling. The optimized method for the HS autosampler was as follows: oven temperature, 70 ℃; valve/loop temperature, 95 ℃; vial equilibration time, 30 min; vial pressurization time, 0.2 min; loop fill time, 0.2 min; loop equilibration time, 0.05 min. Helium drives the headspace to the injection port of the chromatograph via a transfer line at 150 ℃ (2.0 psi flow pressure). The autosampler then pressurizes the vial with helium which forces a portion of the headspace gas mixture through a heated transfer line onto the GC column. The afore-mentioned method exhibits the required accuracy and precision ,

and is characterized by a simple operation of the headspace, a short sample injection period, and good GCMS separation; thus, this method is suitable for analysis of BTEXS in soils.

Concentrations and Spatial Distributions of BTEXS in Surface Soils

Table 1 summarizes the descriptive statistical data for BTEXS concentrations in surface soil samples. In 2013, the total BTEXS concentrations ranged up to 375 ng g^{-1} dry weight, with a median value of 37.5 ng g^{-1}. The median concentration of the 2016 samples was 34.4 ng g^{-1}, with concentrations ranging up to 569 ng g^{-1}. Toluene was the predominant compound, accounting for approximately 41.6 % and 32.1 % of the total BTEXS concentrations in 2013 and 2016, respectively (Fig. S4). Benzene had the second-highest concentration, with a median concentration of 5.13 and 4.36 ng g^{-1}, in 2013 and 2016, respectively, followed by ethylbenzene, *m,p'*-xylene, *o'*-xylene, and styrene. The relative BTEXS ratios were consistent between the two sampling times, suggesting that BTEXS pollution did not dissipate or accumulate between 2013 and 2016 years.

Previous studies examining soils from Shenyang (Pan et al., 2010), Eastern China (Liu et al., 2015) and a pesticide production site in Changzhou (Zhang et al., 2012) have also reported ranges in BTEXS levels consistent with the current study. Toluene levels ranged between 0.61-21.9 ng g^{-1}in Shenyang and average levels of benzene and xylene were 6.62 and 10.9 ng g^{-1}, respectively, in East China. The pesticide production site in Changzhou had comparatively higher BTEX mass concentrations, ranging from 0 to 56.7 <mu>g/g. In addition, the Chinese national BTEXS levels were found to be comparable to other countries, i.e. soils and sediments in Korea have a median BTEXS levels of 55.0 ng g^{-1}(Shin et al., 2012), and

BTEXS levels in sediments near the Morava and Danube rivers in Slovakia are reported to range from 0.02 to 290 ng g^{-1} (Al-Rekabi et al., 1995).

To provide better insight into the spatial variations in soil BTEXS, geological distributions of BTEXS residue levels were mapped across China (Fig. 2). Higher concentrations were found in Shanxi province and Northeast China, as well as Yunnan-Guizhou Plateau. Substantially lower BTEXS levels were found in Southeastern coastal regions, where the lowest concentrations were 1.09 ng g^{-1} in Dalian in 2013 and 2.46 ng g^{-1} in Xiamen in 2016. As shown in Fig. 3, toluene was the most abundant contaminant in more than half of the samples. The sample from Jilin City in Northeastern China was the "hottest" spot for toluene residue, followed by Shuozhou and Taiyuan in Shanxi Province. Interestingly, the spatial tendencies of BTEXS were quite similar to several typical organochlorine pesticides (OCPs). The highest DDT level was found in Shuozhou of Shanxi Province, Northeast China, and Yellow River Valley (Tang et al., 2014). Jilin and Heilongjiang are most polluted by endosulfan, chlordance, heptachlor, and dieldrin at the provincial scale. Guiyang is reported to be a focal point for endosulfans (Niu et al., 2016).

Vertical Distribution Profiles of BTEXS in Soil Column

The vertical distribution profiles of BTEXS in 50 soil cores collected from 2016 are displayed in Fig. 4. The highest concentrations of each individual BTEXS compound were observed in the surface layer the distribution of total BTEXS concentrations in the top (0-15 cm), middle (15-30 cm), and bottom (15-30 cm) soil layers were as follows: 38.8%, 33.5%, and 27.5%, respectively. Concentrations of BTEXS decreased exponentially throughout the depth of the soil columns. In particular, according to one-way ANOVA, there was a significant decreasing trend in

toluene, *m,p'*-xylene, and *o'*-xylene across the top, middle, and bottom layers (toluene: F=5.898, *p*=0.044; *m,p'*-xylene: F=3.257, *p*=0.033; *o'*-xylene: F=5.210, *p*=0.024). However, no significant differences among the soil layers were found for benzene, ethylbenzene, or styrene; the decreasing trend was not as apparent for these compounds.

These findings demonstrate the transport and migration of BTEXS in the soil environment. Firstly, the results suggest an overall slight elevation in residue levels towards the surface. The top soil layer remains the primary pollution site for anthropogenic sources, but BTEXS can leach down along the soil column. We found a decline in toluene, *m,p'*-xylene, and *o'*-xylene from the top soil layer to the bottom, suggesting that these compounds are somewhat restricted in their penetration deeper into the soil column due to lower water solubility and higher K_{ow} values. Benzene has better water solubility (1780 mg L^{-1} at 25℃,101 kPa) and volatility (vapor pressure of 10.1 kPa at 20℃), which increased the vertical transport of benzene among various layers. In addition, the lower level of BTEXS in the deeper column may also result from degradation by anaerobic bacteria. In 2019, Liu et al reported that anaerobic bacteria including *Bacteroidetes*, *Lactococcus*, and *Alcanivorax* played important roles in soil 60-80 cm deep (Liu et al., 2019). In a continuous degradation study, column biodegradation was found to contribute to 69.5% of the reduction in BTEXS from the top to the bottom of the column, along with reduced bacterial growth along the column depth (Karthick et al., 2019). Other studies have reported that significant vertical translocation of hydrophobic organic contaminants (HOCs) may result from the texture of the soil layers. The surface layer is more likely to have clay-sized particles relative to deeper layers; these particles are more easily loaded with HOCs due to their large specific surface (Berknut et al., 2011; Kiersch et al.,

2010). However, the composition of the soil samples was not characterized in the current study; thus, we cannot evaluate this possibility.

Factors Affecting the BTEXS Dispersion and Deposition Pattern

Relationship matrices among the total and individual BTEXS concentrations are displayed in Table 2. Each compound was significantly correlated with one another ($p < 0.01$), suggesting that there are close relationships among these pollutants. The highest correlation coefficient was observed between toluene and total BTEXS (r = 0.920, $p < 0.01$ in 2013; r = 0.899, $p < 0.01$ in 2016). Such finding indicated that total concentration could be an essential factor influencing the residue status of individual compound in soils (Niu et al., 2013).

The main driving factors responsible for the deposition of BTEXS are soil properties and climatic conditions. Organic matter (OM) only constitutes 0.5 -10 % of the soil mass but is intimately associated with soil structure improvement (Serrano and Gallego, 2006). One-way ANOVA indicated that the highest OM group (>25 g kg^{-1}) had significantly higher concentrations of benzene ($p = 0.044$), ethylbenzene ($p = 0.034$), *m,p'*-xylene ($p = 0.01$), *o'*-xylene ($p = 0.039$), and total BTEXS ($p = 0.022$) than the two lower OM groups (Table 3). OM is one of the most important factors controlling the residual levels of BTEXS in agricultural soils because it constitutes the primary sorbent for hydrophobic organic pesticide applications (Pignatello, 1998). Northeast China has the highest BTEXS levels and the highest levels of OM content; this may result from advanced agricultural activities with extensive pesticide applications. In addition, because OM is a mixture of products resulting from microbial and chemical transformations of organic residues (Serrano and Gallego, 2006), microbial biomass is significantly positively correlated with BTEXS in soils

due to the higher levels of microbial activity in soils (Leff and Fierer, 2008). In addition, a number of studies advocate soil pH as the determining factor for solubility of acidic or alkaline VOC compounds based on the isoelectric value evaporation pressure (Insam and Seewald, 2010). Nevertheless, in the current study, there were no significant differences in BTEXS concentrations between the acidic and alkaline samples.

Accumulation of organic pollutants in the environment, particularly the more volatile ones, could be enhanced at sites with higher elevations and lower temperatures due to global distillation effects (Niu et al., 2013). Relatively high BTEXS levels have been detected at Datong basin, which is located at the loess Plateau of Shanxi, where cold condensation is pronounced due to the mountainous topography. In contrast, elevated residue levels in the region of Yunnan-Guizhou Plateau might be attributed to the meteorological parameters, with particular emphasis on the temperature. Table 3 illuminates the direct altitude and temperature dependency. The concentrations of benzene, toluene and total BTEXS were significantly higher in highland regions (elevation > 500 m) than those in plain (elevation ≤ 500 m) at 0.01 levels. Further, there was significant negative association between benzene concentration and annual average temperature with correlation coefficient with *p* value of 0.01.

Wet deposition is considered to be another transportation mechanism influencing the distribution of organic pollutants in the environment (Niu et al., 2013). In this study, only benzene was found to be significantly negatively correlated with annual precipitation ($p = 0.008$). This result can be explained by the solubility of this compound. Among the BTEXS group, benzene displays the highest water solubility (about 1.7 g L^{-1} (at 25℃)). Thus, rainfall patterns may play a crucial role in the

dissipation and transformation of benzene. The solubility of toluene, ethylbenzene, xylene, and styrene is 0.53, 0.2, 0.11, and 0.125 g per liter water at 25℃, respectively. Wet deposition may not play a significant role in the dissipation of these pollutants.

CONCLUSIONS

We undertook a national-scale agricultural sampling campaign in China and elucidated the spatial occurrence and vertical distribution of BTEXS in soils using HS-GCMS. Shanxi and Northeast China, together with Yunnan-Guizhou Plateau, were hotspots for BTEXS pollution. Toluene, *m,p'*-xylene, and *o'*-xylene levels at the soil surface were significantly higher than the levels at greater soil depths. The soil properties and meteorological conditions help to explain the geographic distribution of BTEXS. This systematic analysis of BTEXS behavior in agricultural soils may provide valuable information to assist in better understanding of the risks of such pollutants in arable land across China. Further studies should be focused on BTEXS diffusion from the soil to the air, which would assist in addressing the urgent requirements for emission control policies.

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References

Alghamdi, M. A.; Khoder, M.; Abdelmaksoud, A. S.; Harrison, R. M.; Hussein, T.; Lihavainen, H.; Al-Jeelani, H.; Goknil, M. H.; Shabbaj. I. I.; Almehmadi, F. M.; Hyvarinen, A. P.; Hameri, K. Seasonal and diurnal variations of BTEX and their potential for ozone formation in the urban background atmosphere of the coastal city Jeddah, Saudi Arabia. *Air Qual. Atmos. Health***2014**, *7*(4), 467-480.

Al-Rekabi, H.; Sojak, L.; Kminiak, M. Volatile organic compounds in water and sediment from the Morava and the Danube Rivers (Slovakia) using purge and trap injection and gas chromatography. *Water Air Soil Pollut.***1995**, *81*(1-2), 193-200.

Bergknut, M., Wiberg, K., Klaminder, J. Vertical and Lateral Redistribution of POPs in Soils Developed along a Hydrological Gradient. Environ. Sci. Technol. **2011**, *45*,10378-10384.

Bolden, A.L.; Kwiatkowski, C.F.; Colborn, T. New Look at BTEX: Are Ambient Levels a Problem? *Environ. Sci. Technol.***2015**,*49*(9), 5261-5276.

Campillo, N.; Vinas, P.; Lopez-Garcia, I.; Aguinaga, N.; Hernandez-Cordoba, M.Determination of volatile halogenated organic compounds in soils by purge-and-trap capillary gas chromatography with atomic emission detection. *Talanta***2004**, *64*(3), 584-589.

Du, P.;Sagehashi, M.; Terada, A.; Zhou, S.; Li, F. S.; Hosomi, M. Adequacy of a Simple Diffusion Model to Predict Benzene Behavior in Soil.*Soil Sci. Soc. Am. J.***2011**,*75*(6), 2147-2157.

Fakhari, A. R., Hasheminasab, K. S., Baghdadi, M., Khakpour, A. A simple and rapid method based on direct transfer of headspace vapor into the gc injector: application for determination of btex compounds in water and wastewater samples. Anal. Methods, **2012**, *4 (7)*, 1996-2001.

Fromberg, A.;Nilsson, T.; Larson, B. R.; Montanarella, L.; Facchetti, S.; Madsen, J. O. Analysis of chloro- and nitroanilines and -benzenes in soils by headspace solid-phase microextraction. *J. Chromatogr. A***1996**, *746*(1), 71-81.

Health Canada, Pest Management Regulatory Agency. Regulatory Directive: Formulants Policy and Implementation Guidance Document. **2006**.http://publications.gc.ca/site/eng/289544/publication.html.

Insam, H.; Seewald, S.A. Volatile organic compounds (VOCs) in soils. *Biol. Fertil. Soils***2010**,*46*(3), 199-213.

Karthick, S.; Sangeetha, C.J.; Shashidhar, T. Lab-Scale Biodegradation Study of BTEX under the Unsaturated Condition and Its Effect on Soil Matric Potential. *Soil Sediment Contam*. **2019**, 28(2), 171-183.

Kiersch, K., Jandl, G., Meissner, R., Leinweber, P. Small scale variability of chlorinated POPs in the river Elbe floodplain soils (Germany). Chemosphere **2010**, *79*, 745-753.

Leff, J.W.; Fierer, N. Volatile organic compound (VOC) emissions from soil and litter samples. *Soil Biol. Biochem.***2008,***40* (7), 1629-1636.

Liu, B. H.; Chen, L.; Huang, L. X.; Wang, Y. S.; Li, Y. H. Distribution of volatile organic compounds (VOCs) in surface water, soil, and groundwater within a chemical industry park in Eastern China. *Water Sci. Technol.***2015**,*71*(2), 259-267.

Liu, Q. L., Tang, J. C., Liu, X. M., Song, B., Zhen, M. N., Ashbolt, N. J., Vertical response of microbial community and degrading genes to petroleum hydrocarbon contamination in saline alkaline soil. *J. Environ. Sci.* **2019**, 81, 80-92.

Lu, R.K., Soil and agricultural chemistry analysis (in Chinese). Chinese Agricultural Science Press, Beijing, **2000**.

National Bureau of statistics of China. China Statistical Yearbook;China Statistics

Press, **2013**.

Niu, L. L.; Xu, C.; Yao, Y. J.; Liu, K.; Yang, F. X.; Tang, M. L.; Liu, W. P. Status, Influences and Risk Assessment of Hexachlorocyclohexanes in Agricultural Soils Across China. *Environ. Sci. Technol.***2013**, *47* (21), 12140-12147.

Niu, L. L.;Xu, C.; Zhu, S. Y.; Liu, W. P. Residue patterns of currently, historically and never-used organochlorine pesticides in agricultural soils across China and associated health risks. *Environ. Pollut.***2016**,*219*, 315-322.

Pan, J. S.; Huang, Y.; Yang, Y. L.; Lu, G. H., Wu, X. L.;Wang, X. C. Contamination Distribution of Benzene, Toluene, Ethylbenzene and Xylene in SurfaceWater, Shallow Groundwater and the Adjacent Soils from Shenyang Area. *Res. Environ. Sci.***2010**,*1*(23), 14-19.

Pascale, R., Bianco, G., Calace, S., Masi, S., Mancini, I.M., Mazzone, G., Caniani, D. Method development and optimization for the determination of benzene, toluene, ethylbenzene and xylenes in water at trace levels by static headspace extraction coupled to gas chromatography-barrier ionization discharge detection. J. Chromatogr. A.,**2018**, 1548, 10-18.

Pignatello, J.J. Soil organic matter as a nanoporous sorbent of organic pollutants. *Adv. Colloid Interfac. Sci.* **1998**,*76-77* (2), 445-467.

Pinto, C. G.; Martin, S. H.; Pavon, J. L. P.; Cordero, B. M. A simplified Quick, Easy, Cheap, Effective, Rugged and Safe approach for the determination of trihalomethanes and benzene, toluene, ethylbenzene and xylenes in soil matrices by fast gas chromatography with mass spectrometry detection. *Anal. Chim. Acta*.**2011**,*689*(1), 129-136.

Serrano, A.; Gallego, M. Sorption study of 25 volatile organic compounds in several Mediterranean soils using headspace-gas chromatography-mass spectrometry. *J.*

Chromatogr. A **2006**, *1118*(2), 261-270.

Shin, H. S. Determination of MTBE, TBA and BTEX in Soil by Headspace Gas Chromatography-Mass Spectrometry. *B. Kor. Chem. Soc.***2012**,*33*(5), 1693-1698.

Tang, M. L.; Zhao, M. R.; Zhou, S. S.; Chen, K.; Zhang, C. L.; Liu, W. P. Assessing the underlying breast cancer risk of Chinese females contributed by dietary intake of residual DDT from agricultural soils. *Environ. Int.***2014**, *73* (5), 208-215.

U.S. EPA (United States Environmental Protection Agency)Appendix A to 40 CFR, Part 423--126 Priority Pollutants. **2012**.https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf

U.S. EPA (United States Environmental Protection Agency), Method 5021A: Volatile Organic Compounds (VOCs) in Various Sample Matrices Using Equilibrium Headspace Analysis. **2014**.https://www.epa.gov/hw-sw846/sw-846-test-method-5021a-volatile-organic-compounds-vocs-various-sample-matrices-using.

IARC (International Agency for Research on Cancer). Some Industrial Chemicals and Dyestuffs. vol. 29. WHO Regional Publication,European Series World Health Organization, Regional Office for Europe, Copenhagen. **1999**.http://monographsiarc.fr/ENG/Monographs/vol29/wolume29.pdf

Yao, Y. Spend more on soil clean-up in China. *Nature*.**2016**,*533* (7604), 469-469.

Zeinali, M.; McConnell, L. L.; Hapeman, C. J.; Nguyen, A.; Schmidt, W. F.;

Zhang, L. Z.; Wang,J. R.; Ding, Q.Investigation of Volatile Organic Compounds Contamination in Soil of a Pesticide Production Site in Changzhou. *Environ. Monit. China***2012**,*3*(28), 67-71.

Zhou, Y. Y.; Yu, J. F.; Yan, Z. G.; Zhang C. Y.; Xie, Y. B.; Ma, L. Q.; Gu Q. B.; Li,

F. S. Application of portable gas chromatography-photo ionization detector combined with headspace sampling for field analysis of benzene, toluene, ethylbenzene, and xylene in soils. *Environ. Monit. Assess.***2013**,*185*(4), 3037-3048.

Table 1 Descriptive statistic summary of BTEXS in surface soil samples across China (ng g^{-1})

	mean	min	max	SD[a]	CV[b]	Percentiles		
						25th	50th	75th
benzene	15.8	BDL[c]	136	22.2	1.40	1.31	5.13	22.5
toluene	22.9	BDL[c]	217	28.6	1.25	5.21	13.8	29.3
ethylbenzene	6.53	BDL[c]	46.8	8.11	1.24	1.54	3.93	8.13
m,p'-xylene	4.52	BDL[c]	47.9	6.20	1.37	0.86	2.27	5.99
o'-xylene	2.81	BDL[c]	21.5	3.38	1.20	0.46	1.55	3.85
styrene	2.47	BDL[c]	17.7	3.12	1.26	0.18	1.25	3.51
tBTEXS	55.0	BDL[c]	375	59.3	1.08	13.6	37.5	76.9

(a)

	mean	min	max	SD[a]	CV[b]	Percentiles		
						25th	50th	75th
benzene	7.41	BDL[c]	157	16.9	2.29	2.27	4.36	6.01
toluene	19.5	BDL[c]	213	7.01	1.79	4.00	8.80	18.1
ethylbenzene	9.21	BDL[c]	94.6	2.46	1.34	3.75	5.39	9.89
m,p'-xylene	10.9	BDL[c]	94.8	2.68	1.22	3.72	6.89	12.0
o'-xylene	8.92	BDL[c]	49.0	1.81	1.02	3.66	6.07	9.37
styrene	4.06	BDL[c]	137	2.61	3.24	0.28	1.93	4.48
tBTEXS	60.7	BDL[c]	569	15.5	1.27	23.0	34.4	61.2

(b)

[a] SD: standard deviation

[b] CV: coefficient variation

[c] BDL: below detection level

(a) soil samples from 2013; (b) soil samples from 2016

Table 2 Pearson correlation of individual BTEXS in soil samples

Correlation coefficient	benzene	toluene	ethylbenzene	*m,p'*-xylene	*o'*-xylene	styrene	tBTEXS
benzene	1						
toluene	0.473**	1					
ethylbenzene	0.401**	0.697**	1				
m,p'-xylene	0.425**	0.889**	0.836**	1			
o'-xylene	0.413**	0.803**	0.763**	0.907**	1		
styrene	0.294**	0.501**	0.523**	0.621**	0.652**	1	
tBTEXS	0.741**	0.920**	0.782**	0.892**	0.833**	0.578**	1

(a)

Correlation coefficient	benzene	toluene	ethylbenzene	*m,p'*-xylene	*o'*-xylene	styrene	tBTEXS
benzene	1						
toluene	0.624**	1					
ethylbenzene	0.647**	0.691**	1				
m,p'-xylene	0.384**	0.592**	0.751**	1			
o'-xylene	0.417**	0.490**	0.740**	0.863**	1		
styrene	0.406**	0.304**	0.498**	0.299**	0.274**	1	
tBTEXS	0.706**	0.899**	0.887**	0.795**	0.742**	0.452**	1

(b)

** Correlation is significant at the 0.01 level (2-tailed).

(a) soil samples from 2013; (b) soil samples from 2016

Table 3 Distribution of surface BTEXS levels in relation to environmental parameters

	N	benzene	toluene	ethylbenzene	*m,p'*-xylene	*o'*-xylene	styrene	tBTEXS
OM (g kg^{-1})								
≤17	62	7.69±12.1	18.4±34.4	4.89±5.83	5.52±9.84	4.51±6.92	1.93±2.40	43.2± 50.7
17-25	78	10.4±20.8	18.3±25.8	8.92±13.4	7.94±9.27	6.02±7.30	4.56±15.6	56.4±73.8
>25	87	15.8±23.5	26.1±34.8	8.99±9.70	8.93±12.6	6.44±7.92	3.02± 3.24	69.5±73.7
F test [a]		0.044*	0.205	0.034*	0.010*	0.039*	0.258	0.022*
PH								
≤7	99	9.20±12.6	21.5±30.1	7.99±10.4	7.25±11.8	5.44 ±7.39	2.43 ±2.82	54.1±59.8
>7	128	13.7±24.4	21.2±33.5	7.76±10.5	8.00±10.0	6.03±7.54	3.89±12.4	60.8±75.0
T test [b]		0.076	0.940	0.871	0.604	0.557	0.252	0.470
Elevation (m)								
≤ 500	160	9.03±13.7	18.6±29.8	6.97±9.15	7.59±11.6	5.59±7.51	2.48±2.78	50.6±58.0
>500	67	18.0±29.7	27.4±35.9	9.91±12.9	7.90±8.68	6.29±7.35	5.07±16.8	74.8±87.2
T test [b]		0.002**	0.049*	0.053	0.848	0.515	0.061	0.015*
Temperature (℃)								
≤8	96	15.9±26.8	23.5±37.4	8.23±11.4	7.60±8.74	5.60±6.48	4.87±14.1	65.9±83.4
8-16	85	10.2±14.0	20.1±27.3	7.67±9.77	7.65±13.5	5.99±8.76	1.93±2.33	53.8±58.2
>16	46	5.42±8.50	18.5±26.9	7.32±9.85	7.93±9.49	5.84±6.87	2.24±2.77	47.7±47.8
F test [a]		0.010**	0.625	0.875	0.985	0.937	0.082	0.274
Precipitation (mm)								
≤800	34	23.6±27.4	31.7±47.60	10.8±12.0	10.1±17.1	6.33±8.49	4.58±3.13	87.2±94.9
800-1600	88	10.6±22.1	18.6±31.6	7.27±11.4	6.55±8.02	4.88±6.54	4.59±14.7	52.7±75.5
>1600	105	8.75±13.5	20.0±24.9	7.34±8.92	7.86±10.3	6.39±7.80	1.69±2.28	52.5±47.8
F test [a]		0.001**	0.109	0.186	0.265	0.399	0.072	0.025*

[a] One-Way ANOVA analysis

[b] Independent samples T test

* $p < 0.05$

Figure caption

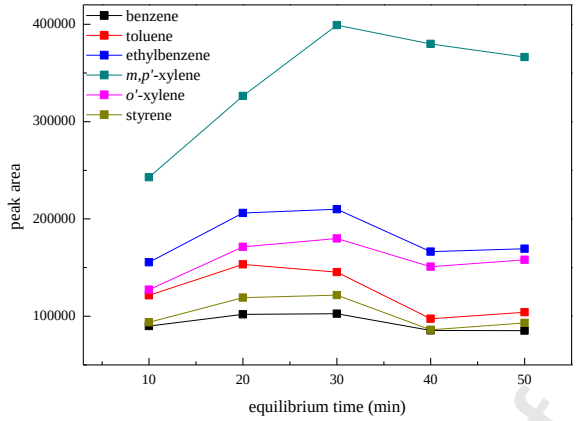
Fig. 1 Optimization of headspace parameters.

Fig. 2 Spatial distribution maps of total BTEXS in rural areas across China, (a) 2013, (b) 2016

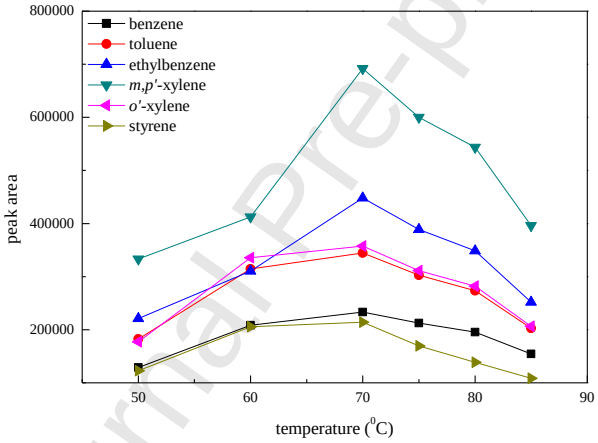
Fig. 3 Spatial distribution of benzene, toluene, ethylbenzene, *m,p'*-xylene, *o'*-xylene and styrene in soil samples from rural China (a) 2013, (b) 2016

Fig. 4 Vertical distribution of BTEXS in agricultural soil column.

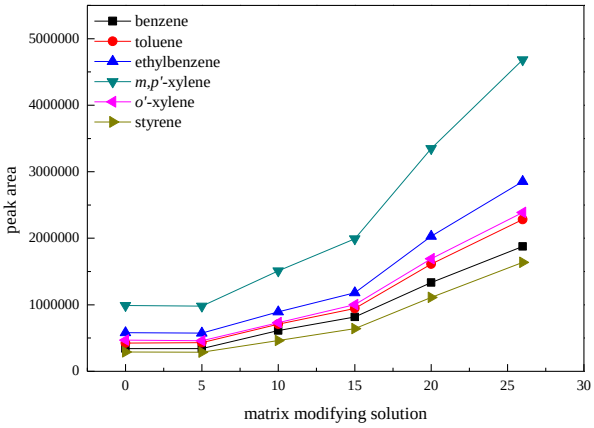
Fig. 1



(a)



(b)



(c)

Fig. 2

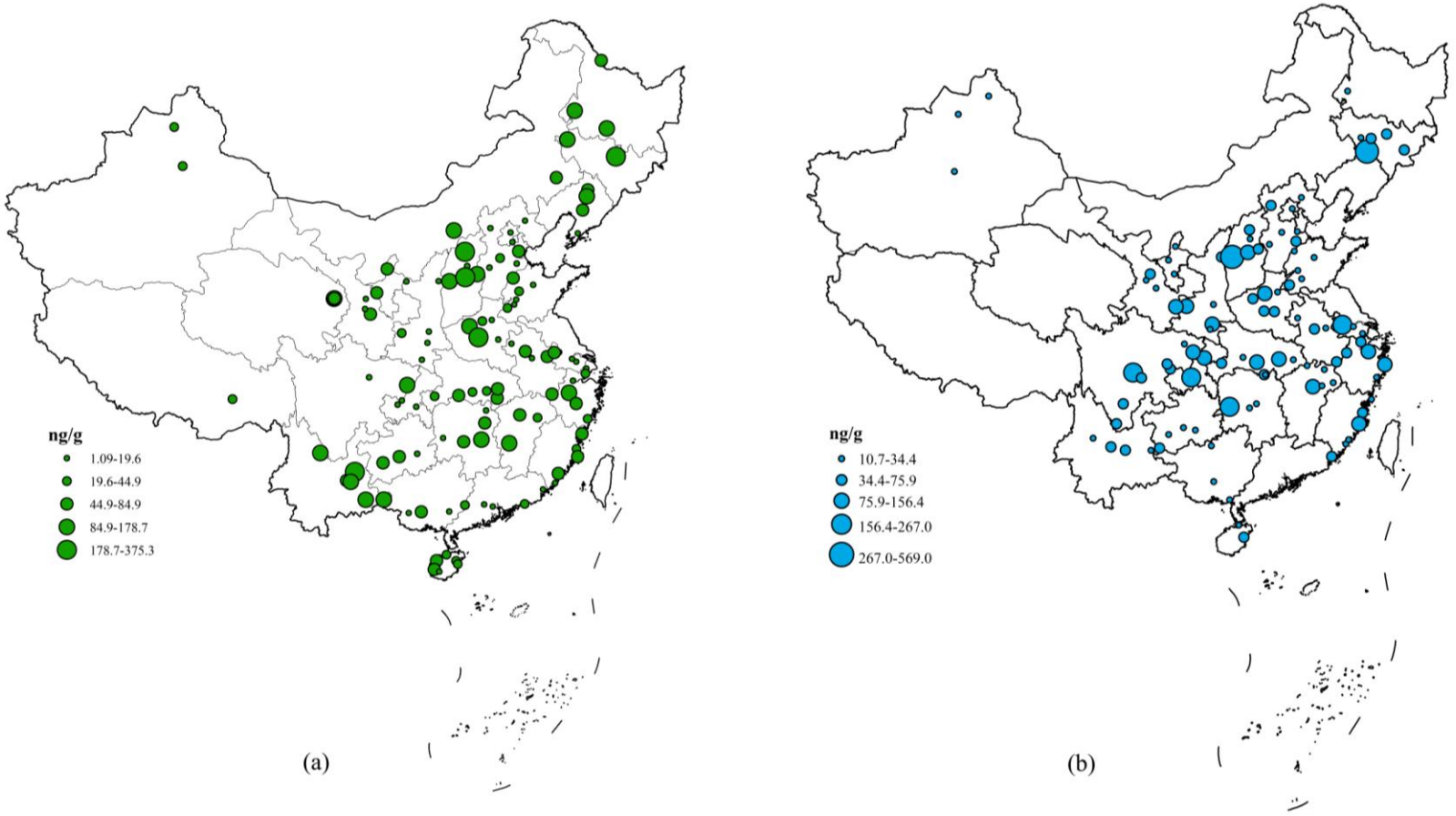

ng/g
1.09-19.6
19.6-44.9
44.9-84.9
84.9-178.7
178.7-375.3
(a)
ng/g
10.7-34.4
34.4-75.9
75.9-156.4
156.4-267.0
267.0-569.0
(b)

Fig. 3

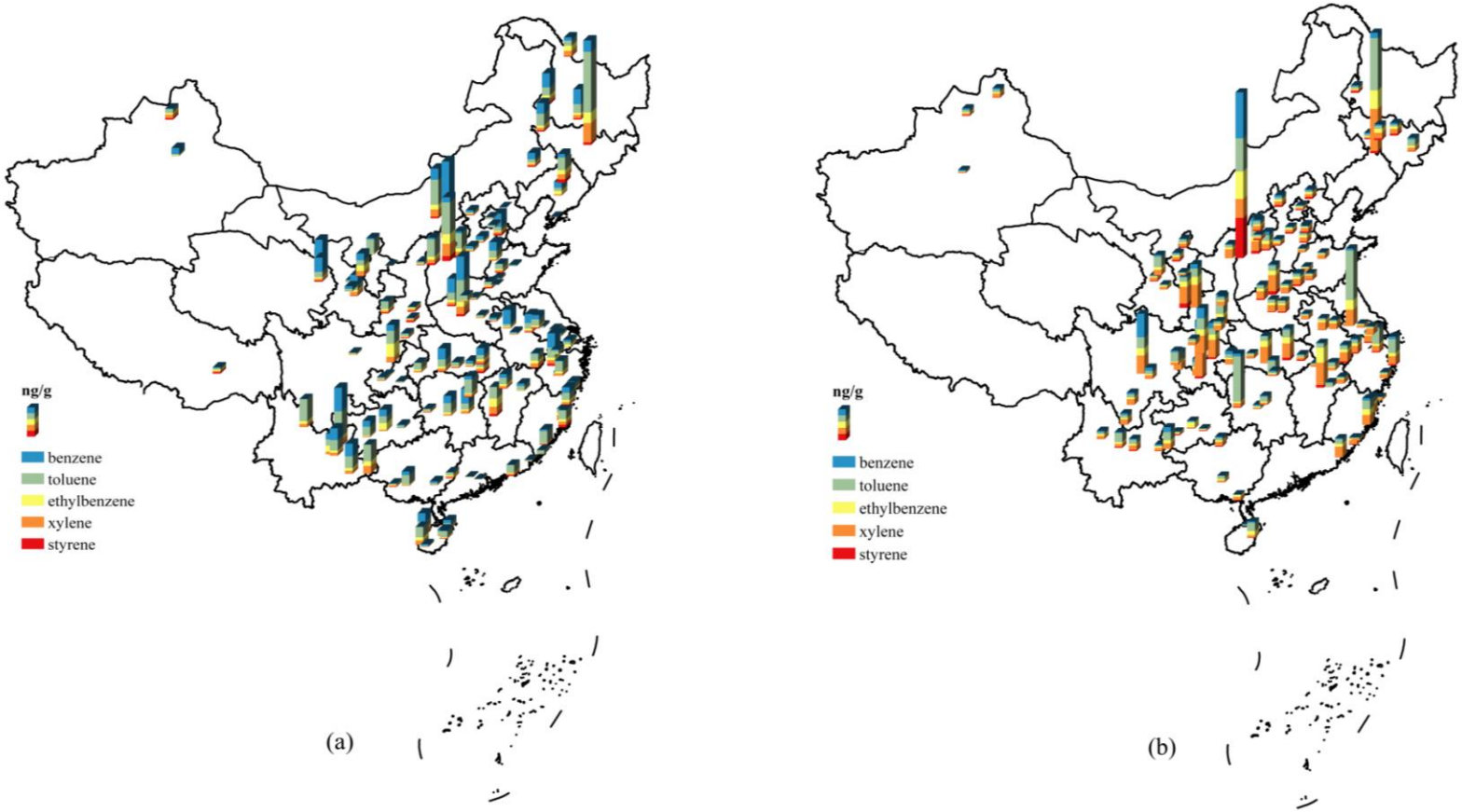
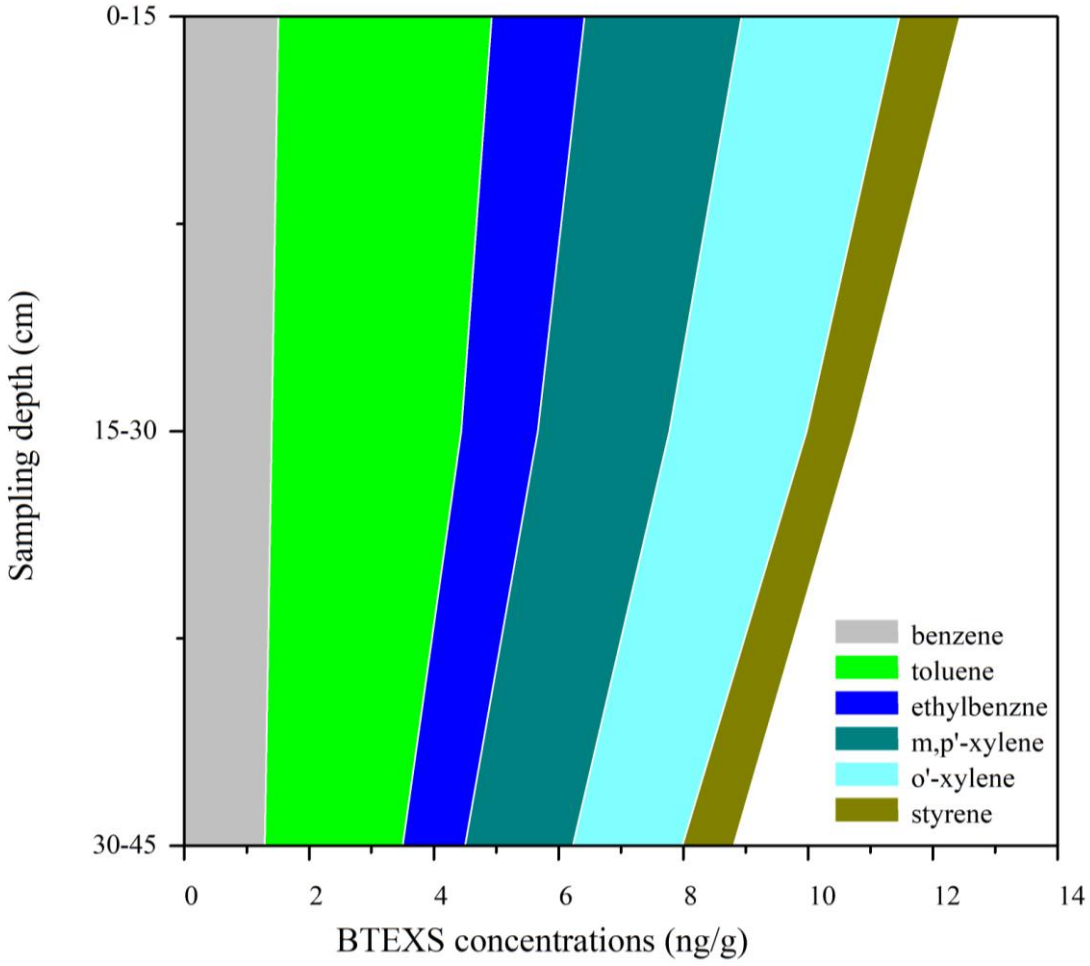
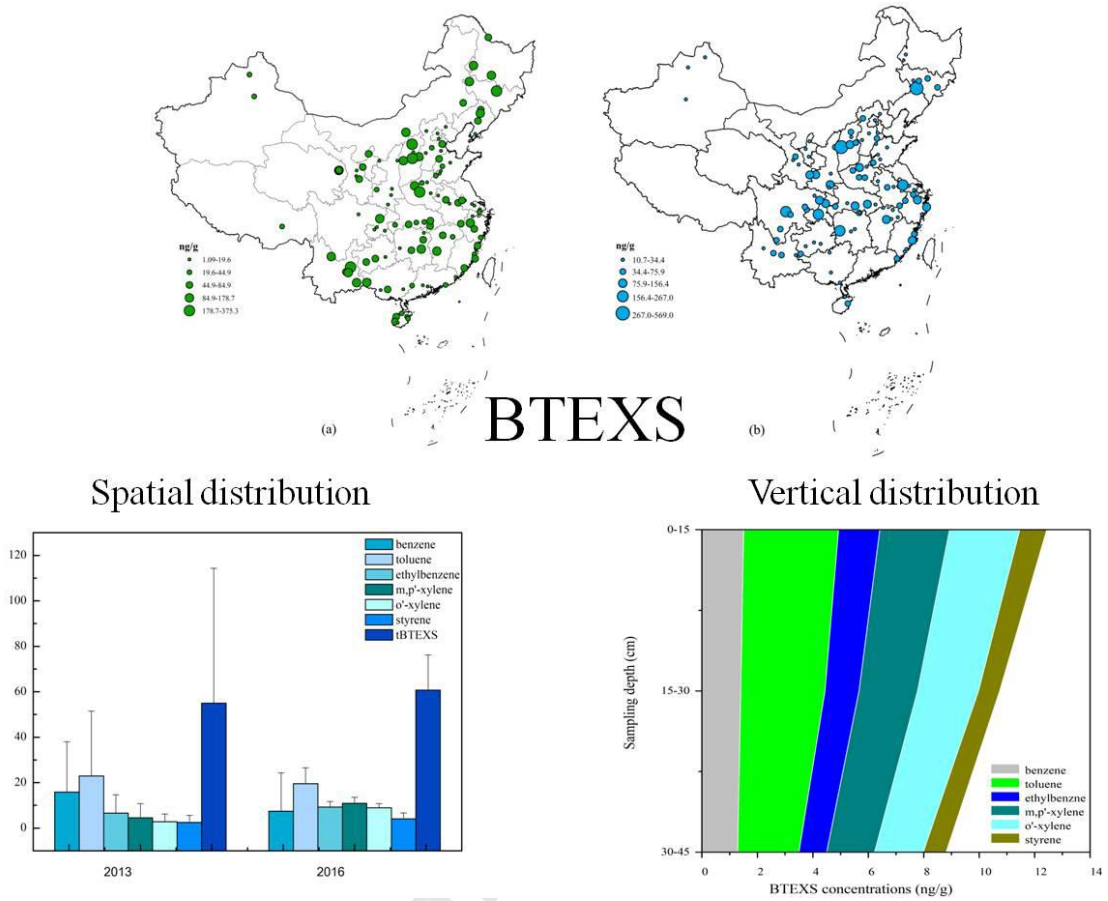

ng/g
benzene
toluene
ethylbenzene
xylene
styrene
(a)
ng/g
benzene
toluene
ethylbenzene
xylene
styrene
(b)

Fig. 4


0-15
15-30
30-45
Sampling depth (cm)
0
2
4
6
8
10
12
14
BTEXS concentrations (ng/g)
benzene
toluene
ethylbenzne
m,p'-xylene
o'-xylene
styrene

Graphical abstract



Highlights

- A sensitive and reliable method for BTEXS determination in soils was established by headspace-gas chromatography-mass spectrometry (HS-GCMS).
- Spatial and vertical distribution of BTEXS in Chinese agricultural soils from 2013 and 2016 were characterized.
- Correlations between BTEXS inventories and anthropogenic activity as well as natural conditions were analyzed to explain the spatial distribution patterns.